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**Original article** 

# Impact of tree species on soil solutions in acidic conditions

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**Abstract** – Capillary solutions of two acidic forest topsoils were sampled for one year. On each of the two soils, there were three stands (Norway spruce, Douglas fir, Hardwood). Capillary solutions were extracted using the centrifugation method. Soil moisture under Hardwood stands was higher than under coniferous stands. Soil solutions under the coniferous tree species were more acidic and more concentrated in  $SO_4^{-2}$ -S and Na<sup>+</sup> than under Hardwoods, showing that coniferous tree species intercept atmospheric depositions more efficiently than hardwood tree species do. Soil solutions under hardwood stands were more concentrated in K<sup>+</sup>, Alt, Si and Fe<sup>3+</sup> than those under coniferous stands. On the least desaturated site, soil solutions under the hardwood stand were less concentrated in NO<sub>3</sub><sup>--</sup>N and C than under the coniferous stands. The amount of rainfall significantly influenced results by diluting soil solutions. When the amount of rainfall was high, there were little difference between tree species.

#### forest soil / tree species / soil solution / centrifugation / acidity

**Résumé** – **Impact des essences forestières sur la composition des solutions du sol en conditions acides.** Les solutions capillaires des horizons superficiels de deux sols forestiers acides ont été échantillonnées pendant une année. Sur chaque sol, trois peuplements étaient présents (Epicéa commun, Sapin Douglas, Feuillu). Les solutions capillaires ont été extraites des sols par centrifugation. L'humidité des sols sous feuillu est supérieure à celle sous résineux. Les solutions de sol sous résineux sont plus acides et plus concentrées en S-SO<sub>4</sub><sup>-2</sup> et en Na<sup>+</sup>, ce qui témoigne d'une plus grande capacité de ces essences à capter les dépôts atmosphériques. Les solutions sous feuillus sont plus concentrées en K<sup>+</sup>, Alt, Si et Fe<sup>3+</sup> que celles sous les résineux. Sur le site le moins désaturé, les solutions sous feuillus sont moins concentrées en N-NO<sub>3</sub><sup>-</sup> et C que celles sous les résineux. La quantité de précipitations influence notablement les résultats en diluant les solutions de sol. Lorsque la pluviosité est très importante, les différences entre essences sont peu marquées.

#### sol forestier / essence forestière / solution du sol / centrifugation / acidité

#### **1. INTRODUCTION**

For more than a century, tree species substitution has been quite a common phenomenom in western Europe. The choice of the tree species planted plays an important role in the functioning of soils [7], particularly the topsoil. In France, two thirds of forests are composed of hardwood stands [34]. After the second world war, large areas were planted with coniferous tree species [34]: initially mainly with Norway spruce (*Picea abies* Karsten.), then with Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco). It is within this context that the present work studied the impact of Norway spruce, Douglas fir, European beech and Sessile oak on soil solutions.

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Soil solutions are important in the functioning of biogeochemical cycles of forest ecosystems as they are the main interface between vegetation, microflora, minerals and organic matters of soil [32]. The composition of soil solutions is the result of processes of production (weathering and mineralisation), deposition (atmospheric deposition; anthropic fertilization and liming) and consumption (by plants and by microorganisms). It is because of their central role that the study of soil solutions gives information on the nutrients available for the vegetation [10] or on the current level of soil acidification [30]. Except for hygroscopic solutions, Titus and Mahendrappa [49] distinguish two types of soil solutions: gravitational solutions and capillary solutions. The first transport existing products down to lower soil depths, whereas the second indicate the balance between the solid, the liquid and the living phases of soil [37]. There are many methods of extracting solutions from soils (see [49] for a review), which have an influence on solution composition. For instance, solutions from zero tension lysimeters are usually less concentrated (except for Al, Si and C) and their pH is lower than solutions extracted by centrifugation [25, 51]. The centrifugation method has the following advantages: it does not necessitate any permanent in situ devices and it extracts capillary solutions, facilitating the study the internal functioning of soils [25].

The objective of this work was to determine the effects of tree species on the characteristics of soil capillary solutions. For this purpose, capillary solutions have been studied for one year using the centrifugation method for one year.

#### 2. MATERIALS AND METHODS

A survey of soil solutions was performed in two acidic forest sites (*table I*): Haye and Remiremont. Both are arboretums established on a forest soil. In each forest, two coniferous stands and one hardwood stand were selected:

- Haye: Norway spruce (*Picea abies* (L.) Karst.), Douglas fir (*Pseudotsuga Menziesii* (Mirb.) Franco), Sessile oak (*Quercus petraea* (Mattus.) Liebl.).
- Remiremont: Norway spruce (*Picea abies* (L.) Karst.), Douglas fir (*Pseudotsuga Menziesii* (Mirb.) Franco), European beech (*Fagus sylvatica* L.).

The hardwood stand represented the forest state before the establishment of the arboretum. The main characteristics of the soils are presented in *table II*. Each stand has a plot size of at least  $1000 \text{ m}^2$ .

Soils were described from a pedological pit. A bulk sample of five soil samples was analysed for each horizon. Horizons were analysed down to 40 cm in depth. The variables were: apparent soil density (cylinder method); particle size distribution (Robinson method); C content [2]; N content [12]; pH (soil:water ratio = 1.25); cationic saturation and cationic exchange capacity [42]; "available" phosphorus [19]; free iron and aluminium [47]. Daily meteorologic data (rainfall, minimum temperature and maximum temperature) were provided by meteorologic stations (Météo-France) near the sites.

Ten samplings were performed during the soil solutions study which was one year long (from April 1998 to April 1999). At each date, nine soil samples were taken in each stand. The nine points were distributed across the entire stand area so as to take into account the high spatial variability of forest soil chemical characteristics [13]. Each point was located under a tree canopy so as to take into account the impact of throughfall [8]. The distance from the point to the nearest trunk was between 1.0 to 1.5 meter because this parameter modifies the impact of throughfall [15] and stemflow [21, 29, 40]. Litter was removed and a stainless steel tube (L = 15 cm ;  $\emptyset = 8$  cm) was vertically driven in. The soil was immediately put in a plastic bag. The hole was filled and its location was marked to avoid its being sampled at a later date. The locations of the samplings were always selected by the same operator. The nine samples were randomly grouped into three bulk samples. At each date, the sampling was performed in a single day and the samples were put in a shaded room at 4 °C. Samples were analysed during the four days following the sampling.

Samples were sieved to 4 mm. Soil water content (in % of dry weight) was measured (drying at 105 °C for 48 hours). Soil solutions were extracted by centrifugation of the samples in cylinders with an internal wall [25]: the internal wall is only permeable to water, preventing the soil sample from reaching the bottom of the cylinder (where the soil solutions collected) during centrifugation. The duration of centrifugation and speed were calculated so as to extract soil solutions up to around pF = 4.2. Preliminary tests have shown that, in such soils, the compositions of solutions extracted up to pF = 3.3 are identical ( $p \le 0.001$ ) with those of solutions extracted between pF = 3.3 and pF = 4.2 (data not presented).

Solutions were filtered (0.45 µm) and homogenized for analysis. pH was measured. Al<sub>t</sub> (Al<sub>t</sub> = total Al), Fe<sup>3+</sup>, Mn<sup>2+</sup>, Si, S, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and PO<sub>4</sub><sup>2-</sup>-P were measured by atomic emission plasma troch spectrophotometry (ICP JY180 Ultrace, Jovin-Yvon). NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N, SO<sub>4</sub><sup>-2</sup>-S and Cl<sup>-</sup> were determined by colorimetry

Table I. $T_{T_{i}}$	Table I. Tree species stands characteristics.	aracteristics.												
Site	Localisation	Bedrock Soil Altitud (generic terms) (F.A.O.) (m)	Soil (F.A.O.)	Altitude (m)	e Rainfall (mm per year) (annual mean)	Rainfall Temperature (mm per year) (°C) (annual mean) (annual mean)	Tree species	Age (year)	Height (m)	$\begin{array}{c} Basal \\ area \\ (m^2  ha^{-1}) \end{array}$	Tree cover (%)	Shrubs cover (%)	Herbs Mosses cover cover (%) (%)	Mosses cover (%)
Haye	plateau of Lorraine silt on (Northeastern France) decarbonatation materials from limestone	e silt on ce) decarbonatation materials from limestone	haplic luvisol	370	760	9.5	Douglas fir Norway spruce Sessile oak	65 65 76*	33.6 28.3 23.3	20 30 30 82 30	65 65 95	$10 \\ 15 \\ 15$	$100 \\ 100 \\ 100$	$\begin{array}{c} 10\\75\\10\end{array}$
Remiremon	Remiremont Vosges mountains (Northeastern France)	s silt on e) sandstone	dystric cambisol	610	1470	8.0	Douglas fir Norway spruce European beech	35 35 190	23.9 21.2 27.7	46 34 21	95 75 85	$\begin{array}{c} 0 \\ 2 \\ 0 \end{array} 0$	1 4 50	$\begin{array}{c} 1\\ 40\\ 1\end{array}$
* Age of standards.	dards.													
Table II. T	Table II. Topsoil horizon characteristics.	acteristics.												
site	tree species t	top soil soil C (cm) density	CL FSi (g / 10	CSi 00 g soil	CL FSi CSi FS CS C (g / 100 g soil (fine earth: < 2mm))	C N 2mm))	$C/N$ $P$ $pH$ $(g kg^{-1})$ water	pH water	H (cm	Na   olc / 100	K C ) g soil (	H Na K Ca Mg Al CEC (cmolc / 100 g soil (fine earth: < 2mm))	Al t: < 2mn	CEC
Haye	Douglas fir Norway spruce Sessile oak	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19.7 26.6 23.4 30.9 25.9 25.9	18.4     19.5     19.5     19.5	34.2 1.1 25.5 0.7 27.5 1.2	2.3 0.14 3.9 0.23 2.9 0.21	16.4 0.00 17.0 0.00 13.8 0.00	4.6 5.4 5.4	0.16 ( 0.16 ( 0.06 (	$\begin{array}{c} 0.02 \\ 0.07 \\ 0.03 \end{array} \begin{array}{c} 0. \end{array}$	0.26 0.65 0.23 0.87 0.36 7.50	55 0.11 37 0.13 50 0.85	$3.40 \\ 4.70 \\ 0.59$	4.6 6.1 9.4

 $CL = clay (< 2 \mu m)$ ;  $FSi = fine silt (2-20 \mu m)$ ;  $CSi = coarse silt (20-50 \mu m)$ ;  $FS = fine sand (50-200 \mu m)$ ;  $CS = coarse sand (200-2000 \mu m)$ .

9.3 7.5 12.0

8.50 6.90 11.00

 $\begin{array}{c} 0.17 \\ 0.14 \\ 0.24 \end{array}$ 

0.08 0.11 0.11

 $\begin{array}{c} 0.27 \\ 0.23 \\ 0.33 \end{array}$ 

 $\begin{array}{c} 0.04 \\ 0.03 \\ 0.03 \end{array}$ 

 $\begin{array}{c} 0.26 \\ 0.10 \\ 0.21 \end{array}$ 

4.1

0.00

18.1 22.1 19.3

 $\begin{array}{c} 0.32 \\ 0.39 \\ 0.71 \end{array}$ 

5.8 8.6 13.7

27.8 25.8 25.4

18.4 16.6 15.0

10.311.2 11.4

21.4 23.9 21.8

22.1 22.5 26.4

 $\begin{array}{c} 0.5 \\ 0.6 \\ 0.5 \end{array}$ 

 $\begin{array}{c} 0-6 \\ 0-5 \\ 0-7 \end{array}$ 

Douglas fir Norway spruce European beech

Remiremont

(TRAACS-2000, Bran-Luebbe). Ionic balance of solutions was defined as follows:

ionic balance = 
$$\frac{\sum \text{positive charges} - \sum \text{negative charges}}{\sum \text{positive charges} + \sum \text{negative charges}}$$

As soils were acidic, Al was considered to be trivalent. Total organic carbon of solutions (DOC, noted here C) was measured (TOC-5050, Shimadzu). Comparative tests between  $SO_4^{-2}$ -S measured by colorimetry and S measured by spectrophotometry showed that all S in solutions was  $SO_4^{-2}$ -S. Therefore, S was measured solely by spectrophotometry and considered to be  $SO_4^{-2}$ -S.

The dataset was stastistically treated with SAS [43]. Variance analysis were performed in "repeated measurements" so as to take into account that data of a temporal series were not independent.

#### **3. RESULTS**

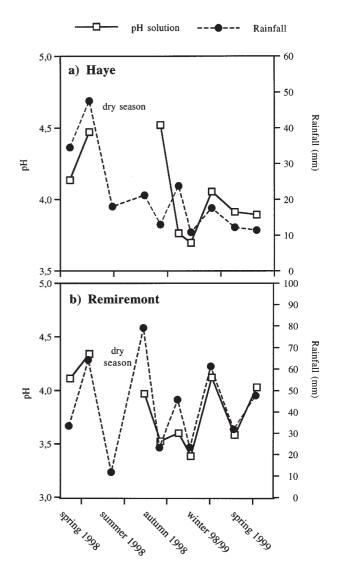
Meteorological data of the studied year (from April 1998 to April 1999) showed that it was slightly warmer and wetter year than the mean year (mean of 30 years).

#### 3.1. Differences between sites

Rainfall was much lower at Haye (813 mm) than at Remiremont (1748 mm). Daily temperature differences (minimum temperature and maximum temperature) between sites were very small. The annual mean differences were less than 1 °C. The annual mean temperature was 10.5 °C at Haye and 10.0 °C at Remiremont. The solution pH was positively correlated (p < 0.001) to the amount of rainfall over the eight days before sampling (*figure 1*). This relationship between pH and rainfall was more clearly expressed at Remiremont (p < 0.001) than at Haye (p < 0.05). The most concentrated solutions were collected in autumn.

At Haye,  $Ca^{2+}$  and  $Al_t$  were the dominant cations, whereas  $Cl^-$ ,  $SO_4^{-2}$ -S and  $NO_3^{-}$ -N were the dominant anions. At Remiremont, H<sup>+</sup>,  $Al_t$  and  $Na^+$  were the dominant cations, whereas  $Cl^-$  and  $SO_4^{-2}$ -S were the dominant anions (*figure 2, table IIIa*).

Soil water content at Haye  $(33.6 \pm 1.1 \text{ g of water for } 100 \text{ g of dry soil}; n = 90)$  was significantly lower (p < 0.001) than at Remiremont  $(56.3 \pm 2.1; n = 90)$ . There was almost no extractable water at Haye at three dates (from June to September 1998) and at Remiremont at one date (July 1998).



**Figure 1.** The relationship between soil solution pH and the amount of rainfalls during the eight days before sampling.

Soil solutions were more concentrated at Haye than at Remiremont (*table IIIa*). Mean solution concentrations at Haye were at least twice those at Remiremont (except for NH<sub>4</sub><sup>+</sup>-N). This difference was particularly large for Ca<sup>2+</sup>, Mn<sup>2+</sup> and NO<sub>3</sub><sup>-</sup>-N. There was no significant difference between sites for solution pH. The [NO<sub>3</sub><sup>-</sup>-N / (NO<sub>3</sub><sup>-</sup>-N + NH<sub>4</sub><sup>+</sup>-N)] ratio was significantly higher (p < 0.001) at Haye (0.89 ± 0.02) than at Remiremont (0.35 ± 0.03).

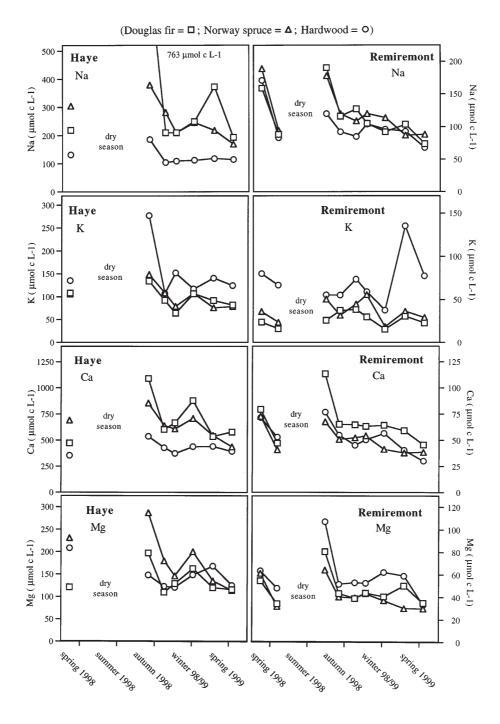
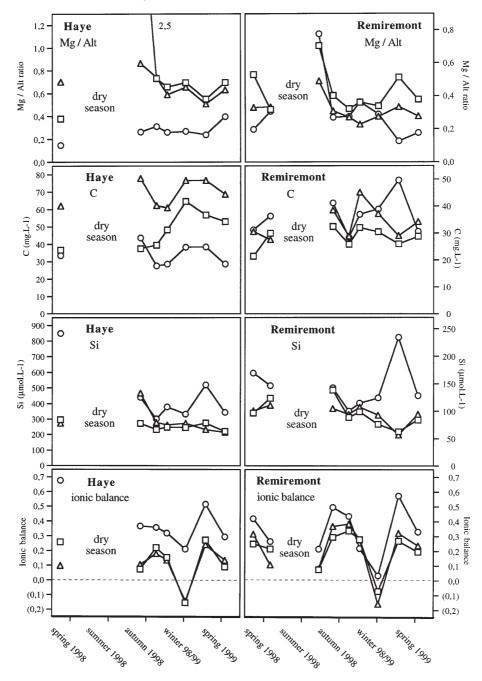


Figure 2. The effect of tree species on soil solution (continued on next page).



(Douglas fir =  $\Box$ ; Norway spruce =  $\Delta$ ; Hardwood = O)

Figure 2. The effect of tree species on soil solution.

Site	Tree species	и	Si ] (µmol L <sup>-1</sup> )	Si NH4-N JIL <sup>-1</sup> )	NO <sub>3</sub> -N SO <sub>4</sub> -S PO <sub>4</sub> -P	SO4-S 1	1	CI-	K <sup>+</sup> (µm	$K^+$ $Ca^{2+}$ $Mg^2$ (µmolc $L^{-1}$ )	±	Mn <sup>2+</sup>	Na <sup>+</sup>	$\mathrm{H}^+$	Alt	Fe <sup>3+</sup> (i	$\mathop{\rm CC}_{(mgL^{-l})}$	Hq	Ca/Alt*	${ m Mg/Al}_{ m *}$
Haye	•	63	332 (32)b	48 (10)ns	381 (40)b	486 (76)b (	5.1 (1.3)b (	479 5 (43)b (	116 (10)b (	585 (41)b (	157 (10)b (	62 (11)b (	234 (32)b (3	167 404 (32)ns (67)b	404 67)b	261 (69)b	51 (4)b (	4.0 (0.1)ns	4.0 1.4 (0.1)ns (0.6)b	0.4 (0.1)ns
Remiremont		81	116 (7)a	41 (6)ns	23 (3)a	155 (16)a (	1.4 (0.4)a (	232 (11)a	45 (5)a	57 (3)a	49 (3)a (i	4.6 (0.4)a	113 (7)a (3	182 (25)ns (	159 (16)a	49 (14)a	34 (1)a (	3.9 0.4 (0.1)ns (0.0)a	0.4 (0.0)a	0.3 (0.0)ns
Table IIIb. ]	Table IIIb. Tree species effect.																			
Site	Tree species	и	Si ] (µmol $L^{-1}$ )	NH4-N	NO <sub>3</sub> -N SO <sub>4</sub> -S	SO4-S 1	PO <sub>4</sub> -P	CI-	K <sup>+</sup> (µm	$K^+$ $Ca^{2+}$ $Mg^{2+}$ $N$	Mg <sup>2+</sup>	An <sup>2+</sup>	$Na^+$	$\mathrm{H}^+$	Al <sub>t</sub>	Fe <sup>3+</sup>	$\mathop{\rm CC}_{(mg\ L^{-l})}$	Hd	Ca/Al <sub>t</sub> *	${ m Mg/Al_t}_*$
Haye	Douglas fir	21	256 (10)a	30 (7)ns	445 (52)b (	509         3.5         521         97           (151)ab (1.7)ns (107)ns (8)ns	3.5 1.7)ns (	521 107)ns	97 (8)ns	691 (82)b (	137 (12)ns (	60 9)ab	317 (78)b ((	188 (61)ab (	216 (37)a	107 (48)a	48 (4)ns	3.9 (0.2)b	3.2 (1.5)b	0.6 (0.3)ns
Haye	Norway spruce	21	286 (31)a	61 (24)ns	499 (65)b (	672 (135)b (	b (1.8)ns (51)ns (1	469 51)ns (	100 (0)ns	642 (50)b (;	185 (23)ns (	116 (12)b (	258 (26)b (	268 (48)b (	276 (20)a	76 (28)a	69 (3)ns	3.6 (0.1)b (	2.3 (0.1)ab	0.7 (0.0)ns
Haye	Hardwood (Sessile oak)	21	452 (72)b	53 (18)ns	199 (30)a	275 (58)a ((	7.6 447 (2.8)ns (63)ns	447 63)ns (	150 22)ns	424 (23)a (	149 (12)ns	11 (2)a (	125 (11)a	47 (9)a (	721 (131)b	599 (126)b	34 (2)ns	4.4 (0.1)a	0.6 (0.1)a	0.2 (0.0)ns
Remiremont	Douglas fir	27	103 (10)ns	32 (6)ns	26 (4)ab	146 (22)ns ((	i 1.2 is (0.6)ns (	221 19)ns	27 (3)ns	67 (7)ns (	47 (5)ns ((	5.7 (0.6)ns (	117 s (12)ns (-	168 (43)ns	110 (4)a	21 (2)ns	29 (1)ns (	3.9 (0.1)ns	0.6 (0.1)b	0.4 (0.0)ns
Remiremont	Norway spruce	27	99 80(9)	45 (16)ns	11 (2)a	166 (35)ns ((	1.4 (0.7)ns (	243 (20)ns (	36 (4)ns	51 (4)ns (	42 (4)ns ((	3.6 (0.5)ns (	122 (12)ns (-	197 (49)ns (	133 (12)a	25 (4)ns	35 (2)ns (	3.8 (0.1)ns (	0.4 (0.0)ab	0.3 (0.0)ns
Remiremont	Hardwood (European beech)	27	145 (3)ns	47 (9)ns	31 (8)b	153 (25)ns ((	1.7 231 (0.9)ns (16)ns		71 (9)ns	53 (5)ns (	59 (7)ns ((	4.4 (0.7)ns (	101 (10)ns (-	183 (40)ns (	235 (36)b	101 (37)ns	37 (2)ns (	3.8 (0.1)ns	0.2 (0.0)a	0.3 (0.1)ns

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Table IIIa. Site effect.

Values followed by different letters differ significantly at the 0.05 probability level (ns = no significant difference). \*: Ca, Mg and Al<sub>t</sub> in cmol c  $L^{-1}$ .

#### 3.2. Differences among tree species

#### Haye:

During soil sample sieving, it was noted that there were quite numerous earthworms in Sessile oak soil whereas none were present in Douglas fir and Norway spruce soils. Some ant-hills were observed in the Norway spruce stand.

Soil moisture was significantly higher (p < 0.05) under Sessile oak ( $35.1 \pm 1.0$  g of water for 100 g of dry soil) and under Norway spruce ( $36.0 \pm 2.2$ ) than under Douglas fir ( $29.7 \pm 1.3$ ). The pH of soil solutions under hardwood stand was at least 0.5 unit higher than under coniferous stands (*table IIIb*). Solution concentrations of SO<sub>4</sub><sup>-2</sup>-S and Na<sup>+</sup> were lower under hardwoods than under Norway spruce and Douglas fir (*table IIIb*). NO<sub>3</sub><sup>--N</sup> concentrations and [NO<sub>3</sub><sup>--N</sup> / (NO<sub>3</sub><sup>--N</sup> + NH<sub>4</sub><sup>+-N</sup>)] ratios were lower under hardwood stand than under coniferous stands. Such was also the case for Ca<sup>2+</sup> concentrations and Ca/Al<sub>t</sub> ratios. Si, Fe<sup>3+</sup> and Al<sub>t</sub> concentrations were higher under hardwood stand than under coniferous stands. Mn<sup>2+</sup> concentrations of solutions were higher under Norway spruce than under hardwoods.

There was no statistically significant differences among tree species for the other variables. However, there were some tendencies for K<sup>+</sup> (*figure 2a*) as well as for Mg/Al<sub>t</sub>, C and ionic balance (*figure 2b*). It seems that K<sup>+</sup> concentrations were higher under hardwoods than under coniferous species. This was also the case with the ionic balance. In contrast, solutions under hardwoods had lower values of C concentration and of Mg/Al<sub>t</sub> ratio than under coniferous species. Ranked according to C concentration, tree species were as follows: Norway spruce > Douglas fir > Sessile oak.

#### **Remiremont:**

Soil samples from the European beech stand contained a few more arthropoda than samples from coniferous stands. Soil moisture was significantly higher (p < 0.05) under European beech than under Norway spruce and Douglas fir (respectively:  $66.9 \pm 3.6$  g of water for 100 g of dry soil,  $52.3 \pm 2.2$  and  $49.6 \pm 1.9$ ). The tree species effect on the composition of soil solutions was not nearly so clearly expressed at Remiremont as at Haye (table IIIb). There were significant differences (p < 0.05) only for NO<sub>3</sub><sup>-</sup>-N, Al<sub>t</sub> and Ca/Al<sub>t</sub> ratio. Compared to coniferous species, hardwood had higher values for NO<sub>3</sub><sup>-</sup>-N and Al<sub>t</sub>, and lower values for the Ca/Al, ratio. Although results were not statistically significant for the other variables, it seems that there were some differences for  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  (figure 2a) as well as for Mg/Al, ratio, Si and ionic balance (*figure 2b*). Hardwood had higher values than coniferous species for  $K^+$ ,  $Mg^{2+}$ , Si and ionic balance. Douglas fir had the highest concentrations of  $Ca^{2+}$  and seems to have a higher Mg/Al<sub>t</sub> ratio than Norway spruce.

#### 4. DISCUSSION

The pH of capillary solutions extracted from topsoils was statistically linked to the amount of rainfall. The more the rainfall, the higher the soil solution pH. The measurements made in the "national network for the long-term monitoring of forest ecosystems" (RENECO-FOR) showed that rainfall pH in the area of the present study was between 5.0 to 5.5 [50]. This pH is higher than those of soils (*table II*). When the amount of rainfall was high, soil solutions were less acidic as they contain a lot of solution with quite high pH [20]. The effect of rainfall on soil solution pH was more clearly expressed at Remiremont than at Haye because the rainfall at Remiremont was more than twice that at Haye.

Only one year of monitoring was available. Therefore, it is difficult to show a seasonal trend in the results. However, it seemed that the summer dessication tended to concentrate the soil solutions.

Soil moisture at Remiremont was higher than at Haye because of the higher quantity of rainfall and of the more homogeneous soil particle size distribution (*table II*). Soil solutions at Haye were more concentrated than those of Remiremont. Although rainfall had low concentrations [50], the difference in concentrations can not be explained solely by the difference of rainfall amounts, especially  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$  and N. For these elements, it is probable that the Haye bedrock (silt on decarbonatation materials from limestone) produced more calcium and easily weathereable minerals than the Remiremont bedrock (silt on sandstone).

Soil moisture was higher under hardwoods than under coniferous species: hardwoods  $\geq$  Norway spruce  $\geq$  Douglas fir. Nihlgard [35] and Benecke and Mayer [4] have already shown that soils are drier under Norway spruce than under European beech. This behaviour was due to the higher ability of coniferous tree species to intercept rainfall [3, 24].

In contrast to Haye, Remiremont showed few differences in soil solution composition among tree species. However, other authors have established that tree species modify the composition of soil solutions (e.g. [1, 14]). The results from the Remiremont site can be explained by two phenomena: (i) the very high amount of rainfall at Remiremont diluted soil solutions and hid the tree species effect. (ii) as the soil was more desaturated than at Haye (saturation index for exchangeable earth-alkaline

References	Localisation	Soil depth (cm)	Tree species	рН	Ca (J	Mg umol L⁻	$(Al_t)$	Al inorganic (Al <sub>i</sub> )	$Al_i / Al_t$	Ca / Al <sub>t</sub>	Mg / Al <sub>t</sub>	Ca / Al <sub>i</sub>	Mg / Al <sub>i</sub>
[22, 23]	Sor catchment	0.10	Pinus sylvestris Pinus sylvestris	4.4 4.5	50 45	41 78	41 65	33 58	0.8 0.9	1.2 0.7	1.0 1.2	1.5 0.8	1.2 1.3
[22, 23]	(Spain)	0-10	Quercus robur Quercus robur	4.4 4.4	60 135	70 144	75 153	37 76	0.5 0.5	0.8 0.9	0.9 0.9	1.6 1.8	1.9 1.9
[17]	Sahnaahana	0–5	Picea abies	3.3	98	25	62	41	0.7	1.6	0.4	2.4	0.6
[17]	Schneeberg (Germany)	0–5	Fagus sylvatica	3.6	125	33	70	24	0.3	1.8	0.5	5.2	1.4
[17]	Cilarada a d	0.5	Picea abies	3.4	267	66	163	96	0.6	1.6	0.4	2.8	0.7
[17]	Silverbach (Germany)	0–5	Fagus sylvatica	3.7	181	45	128	90	0.7	1.4	0.4	2.0	0.5

Table IV. The effect of tree species on aluminum speciation in soil solution.

cations at 5 cm depth: Remiremont = 7%; Haye = 46%), the buffering capacity of Haye was more sensitive and thus influenced by the impact of tree species on the environment.

At Haye, soil solutions under Norway spruce and Douglas fir were more concentrated in  $SO_4^{2-}$  and  $Na^+$ than those under hardwoods. It has been established that the origin of these elements in acidic soils was mainly atmospheric [26]. It suggested that Norway spruce and Douglas fir intercepted the atmospheric deposition more than Sessile oak do. Brown and Iles [14], Ranger and Nys [38] and Berkvist and Folkesson [5] have measured the extent to which coniferous species (Picea abies, Pinus sylvatica) intercept atmospheric deposition more than hardwood species do (Quercus petraea, Fagus sylvatica, Betula pendula). It is probable that the high soil solution concentrations of NO3-N and Ca2+ under coniferous species were partly due to high atmospheric deposition. Thus, on an acidic soil of northeastern France, Ranger and Nys [38] have reported that a Norway spruce stand intercepted 155% more N than a Sessile oak stand, 50% more S, 10% more Ca but 15% less K. It should be noted that the age of the hardwood stand at Remiremont could have masked this effect (table I). Indeed, Hugues et al. [27] have shown with several Picea sitchensis chronosequences that atmospheric deposition to canopies increases with stand age. Furthermore, the introduction of exotic tree species, such as Norway spruce and Douglas fir, could have led to mineralisation of old organic matter in soil and, then, to higher nitrification flux. This hypothesis was suggested by Jussy et al. [28], but still need a validation.

The pH of soil solutions at Haye were tree species dependent. There was at least 0.5 unit difference between the solutions of harwoods and those of coniferous tree species. The effect of tree species on solution pH was as follows: Sessile oak > Douglas fir  $\geq$  Norway spruce. This result is due to the higher ability of coniferous tree species to intercept atmospheric deposition, which is potentially acidic. Soil solutions were more acidified under coniferous species than under hardwoods also because of the low pH of coniferous species needles [36] and the more acidic organic matter of Norway spruce [46]. The acidity of the coniferous stands at Haye could prevent burrowing fauna, such as earthworms, from colonizing the soil [16]. Root exudates could have influenced the results as they are tree species dependent [45].

For both sites, soil solutions were more concentrated in  $K^+$  under hardwoods than under coniferous species. This difference in behaviour for  $K^+$  between hardwoods and coniferous species has been mentioned in a composition study on artificial soil [48]. The K contents of Sessile oak and European beech leaves are 50% higher than those of Norway spruce and Douglas fir needles [6, 9]. Therefore, processes like litter mineralisation and foliage recretion could have promoted a higher concentration of this element under hardwood species than under coniferous species.

The high concentrations of  $Mn^{2+}$  in Norway spruce soil solutions compared to hardwood solutions were due to soil solution pH. Indeed, this element is soluble in acidic solution [20]. At Haye, the tree species effect on the C content of soil solution was the inverse of its effect on pH: Norway spruce  $\geq$  Douglas fir  $\geq$  Sessile oak. Raulund-Rasmussen et al. [39] have also shown that the C content of soil solution was: Norway spruce > European beech = Pedunculated oak. As previously stated, this could be the result of an enhanced mineralisation of old soil organic matter which increases the soil acidification under coniferous tree species. It should be underlined that C content of solutions is correlated to its ability to alter minerals [39]. Nevertheless, as concentrations of Si was also highest in Sessile oak soil solutions, it cannot be concluded that the weathering rate of soil minerals under Norway spruce was higher than under Sessile oak.

At Have, as at Remiremont, soil solutions under hardwoods showed a larger ionic inbalance (positive balance) than under coniferous species. For the present study, Al was considered as  $Al^{3+}$  because solutions were acidic. Solutions pH could explain the results of Haye as Al speciation is pH dependent [41]. Indeed, Driscoll [18] has shown that, in solutions with organic matter, Al<sup>3+</sup> represented 100% of  $Al_t$  at pH = 3.6 (pH of soil solutions under Norway spruce), 90% of Al<sub>t</sub> at pH = 3.9 (Douglas fir), but only 50% at pH = 4.4 (Sessile oak). Moreover, for soil solutions at pH = 4.4, Fernandez-Sanjurjo et al. [23] have shown that only 20% of Al<sub>t</sub> was in the Al<sup>3+</sup> chemical form. Therefore some Al in hardwood soil solutions may not be trivalent. This has led to an overestimation of the total positive charge of solutions under hardwoods. Nevertheless, soil solutions under the hardwood stand at Remiremont were also unbalanced, though no less acidic than those under the coniferous stands. This situation suggested that hardwood stands did have not the same Al speciation as coniferous stands. Thus, according to literature data (table IV), it seems that the (inorganic Al i.e. almost  $Al^{3+}$ ) /  $(Al_t)$  ratio is often lower under hardwood stands than under coniferous stands (except at Silverbach, [17]). If such was the case at Remiremont, it would explain the imbalance of the European beech solutions. It is possible that the phenomena which have led to modification of the Al speciation under the hardwood stands have also enhanced the solubilization of Al, Fe and Si (table IIIb). These processes are probably dependent on biological cycles, as Si and Al fluxes in forest ecosystems are partly controlled by tree litter [31]. For the present study, Ca/Al, and Mg/Al, ratios of hardwood solutions were lower than those of coniferous species solutions. Such was also the case of Skeffington [44]. But Brown and Iles [14] and Koch and Matzner [29] have shown the opposite results. Ca/Al<sub>t</sub> and Mg/Al<sub>t</sub> ratios are often used as indicator values of the potential toxicity of Al for vegetation on very desaturated soils [33]. However, only few forms of Al are toxic (mainly  $Al^{3+}$ ). Therefore,  $Ca/Al_t$  and  $Mg/Al_t$  ratios are not efficient indicators of potential Al toxicity [10] because they do not take into account the Al speciation [11]. It should be observed that the tree species gradient for Ca/Al and Mg/Al ratios is reversed when only inorganic Al (i.e. almost  $Al^{3+}$ ) is considered, instead of total Al (*table IV*). Thus, Al<sub>t</sub> is not a efficient index of Al toxicity and, therefore, it is difficult to discuss the ecological meaning of the ratios of the present study.

#### **5. CONCLUSION**

The pH and the composition of capillary solutions of topsoils were highly dependent on the amount of rainfall. The bedrock characteristics were also an important factor controlling the chemistry of capillary solutions.

The tree species effect on topsoil solutions was small when the amount of rainfall was high. Exotic coniferous tree species intercepted rainfall and atmospheric deposition more readly than did native hardwoods. This situation led to a decrease in soil water content and to an acidification under coniferous stands. It is also probable that the introduction of coniferous tree species has modified the biogeochemical cycles of some elements, such as K, N or Al, in the ecosystems, suggesting different nutrition modes according to tree species. Complementary works are required to determine the tree species effect on the long term fertility of acidic soils. These works should concern the study of gravitational solutions so as to measure the impact of tree species on the amounts of elements lost by drainage.

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